PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 20/00, 283/00 | A1

(11) International Publication Number: WO 95/09875

(43) International Publication Date: 13 April 1995 (13.04.95)

(21) International Application Number: PCT/US94/11254

(22) International Filing Date: 4 October 1994 (04.10.94)

(30) Priority Data:
08/132,530 6 October 1993 (06.10.93) US

(71)(72) Applicant and Inventor: HAMMOND, Warren, Scott [US/US]; 138 Lake Shore Drive, Lake Park, FL 33403 (US).

(74) Agent: HALEY, Barry, L.; Malin, Haley, DiMaggio & Crosby, P.A., Suite 1609, One East Broward Boulevard, Fort Lauderdale, FL 33301 (US).

(81) Designated States: AU, BB, BG, BR, CA, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: COMPLEX THERMOSET POLYMER COMPOSITION

(57) Abstract

A composition comprising a liquid epoxy resin and a liquid polyeser resin and a liquid epoxy hardener curable at room termperature to produce a cross-linked polymer suitable for multiple construction uses. The composition may also be used as a lamina readily bondable to expanded styrene to form laminates of expanded styrene having a protective, rigid coating surrounding the entire styrene package which enhances and increases the strength of the expanded styrene, for example for use as structural elements. The composition may also include fillers such as silica sand for simulated tile and stucco surfaces of improved strength, and conventional fillers such as fire retardants and ultraviolet protectants. The composition may be formulated to provide a flexible material for use as a simulated vinyl or rubber-like material. The composition is also useful as a bonding agent, particularly for bonding expanded styrene foam or polyester based materials to epoxy-based materials.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

COMPLEX THERMOSET POLYMER COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a composition comprising an epoxy resin cross-linked with a polyester resin. The product is especially useful as a structural element as a flexible to rigid sheet, or laminated with another material particularly expanded styrene. The composition bonds readily to expanded styrene and can be cured and cross-linked at room temperature in the presence of known hardeners for epoxy resins. The product is also useful as a bonding agent and adheres epoxy materials to polyester materials.

2. Description of the Prior Art

Epoxy resin has been used in many ways, typically as a clear protective coating, for numerous construction materials. Epoxy resins comprise thermosetting homopolymers or copolymers containing epoxy groups which are characterized by toughness, strong adhesion, and high corrosion and chemical resistance, and are especially used in surface coatings and adhesives.

Polyester resins comprise synthetic polymers produced by the reaction of poly basic acids with polyhydric alcohols. Reinforced polyester resins are strong, light and weather resistant, and are often used in boat hulls, swimming pools, waterproof fibers, adhesives, and molded parts. Epoxy resins and polyester resins have been used independently in many ways for structurally reinforced products, and often are combined with additives such as ultraviolet stabilizers and fire retardants.

SUMMARY OF THE INVENTION

The present invention provides an improved composition comprising an epoxy resin cross-linked with a polyester resin capable of a variety of uses, such as a material that simulates a number of molded plastics, typically demonstrating cost effective, superior properties. The composition also has superior bonding properties, particularly to expanded styrene, polyesters, and epoxies. The resulting laminates are exceptionally useful as a relatively inexpensive strong, weather resistent material with particular advantages as structural elements. The laminated product can be formulated for rigidity, high wear resistance, and high structural value, or other desired properties. The compositions of the invention can also be reinforced with fiberglass or other fibers to produce a higher structural element, with or without a foam core such as expanded styrene, or other lamina. Fillers such as silica sand, or colorants, or fire retardant additives are readily incorporated into the composition to vary the properties thereof.

DETAILED DESCRIPTION OF THE INVENTION

The composition of the invention comprises a liquid epoxy resin and a liquid polyester resin admixed in predetermined proportions as described below with an epoxy hardener only for reaction at room temperature and atmospheric pressure to provide a cured cross-linked epoxy/polyester solid matrix. No additional energy such as heat or electric energy is necessary to obtain the product.

In a first embodiment, the quantities of epoxy resin and polyester resin are selected for use in conjunction with an appropriate hardener for epoxy resins of known characteristics to obtain desired properties in the resultant thermoset plastic, such as high strength, light weight, rigidity, and/or flexibility.

Another significant use of the present invention is that with the proper additives, such as silica sand, sodium

bicarbonate, or other conventional materials, the epoxy and cross-linked polyester resins, in combination with the appropriate hardeners, can be formulated to provide a product which simulates other materials, such as synthetic ceramics or stone surfaces in a very cost effective way. Compositions comprising over 60% filler by volume can be formulated without significantly affecting the strength of the product.

In another embodiment, a cross-linked epoxy/polyester lamina is applied to expanded styrene as a structural protective sheet. For example, the epoxy polyester blend plus hardener is applied to a 4 ft. by 8 ft. by 1 in. sheet of expanded styrene and cured to provide a high strength, low cost laminate that can be used in the creation of innumerable products, including structural elements for residential and commercial construction. Laminates according to the invention typically comprise cross-linked epoxy/polyester lamina of at least about 1/32 inch thickness depending on the desired strength of the laminate.

The improved composition, which produces a sturdy, rigid, plastic material that can simulate many products, can for example include an epoxy resin such as bisphenol-A-polyglycidyl ether in proportion with a polyester resin such as a general purpose, commercially available resin with less than about fifty percent (50%), preferably 30% styrene monomer (depending on the intended utility) and a fast epoxy hardener such as an amino ethyl peperzaine accelerated by nonyl phenol, all of which may be blended at room temperature and atmospheric pressure. In one example, eight parts epoxy resin, two parts polyester resin, and five parts fast epoxy hardener are combined. Optionally, additives such as fire retardants, stabilizers, or fillers such as silica sand can be utilized. The rigidity of the resultant composition and the material so formed can vary greatly by varying the parts by volume of the composition mixture to produce a very hard material or a soft, rubber-like material without additives such as elastomerics. One of the great advantages of the present invention and the basic composition provided herein of a cross-linked polyester resin with an epoxy

resin and a hardener as a laminate for expanded styrene is its low cost, combined with extreme structural rigidity owing to its superior bond, with expanded styrene, unattainable by other thermoset products.

It is an object of this invention to provide a new and improved composition of matter that includes a blend of liquid polyester resin, liquid epoxy resin and hardener, optionally in combination with a low-thinner co-solvent for the resins.

It is another object of this invention to provide a composition comprising epoxy resin, polyester resin, and hardener for the production of improved construction materials useful for all types of construction.

Yet another object of this invention is to provide a composition comprising a bonding agent including polyester resin and epoxy resin blend mixed with hardener, and optional fillers, useful for various forms of construction elements similar to those comprising known thermoset plastics which is compatible with thermosets such as styrene, polyol-based polymer products, and epoxy products, incompatible by nature.

And yet another object is to provide a new composition that has improved bondability to expanded styrene as a structural sheet without significant impairment of the expanded styrene foam substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention comprises a composition for the production of a useful construction material for various articles comprising an epoxy resin combined with a polyester resin in sufficient predetermined quantities with sufficient epoxy hardener to cure and cross-link the resins.

Secondly, the composition is also suitable for use as a sheet that readily bonds with expanded styrene to produce a very low cost construction material that has numerous uses and applications for the construction of all types of useful articles.

Thirdly, the composition may also be used with fillers to provide for ultraviolet light stabilization, flame retardancy, color, or other fillers for simulating construction materials such as synthetic ceramics or brick including silica sand and other types of reinforcing agents, including fibers such as fiberglass.

Epoxy resins with epoxy hardeners used in the invention consist of those compositions which in the presence of polyesters, function to cure the polyesters as well. Preferred hardeners comprise those which inherently provide sufficient reaction energy to cure both epoxy and polyester precursors without additional energy input such as an amino ethyl peperzaine accelerated by nonyl phenol (e.g. Eputoph 37610 marketed by Reichhold, 425 South Place Blvd., Pensacola, Florida 32596) that create a sufficient high heat in the epoxy/polyester curing process and eliminate any necessity for additional heat or curing agents. The cured, cross-linked composition of the invention can thus be obtained at room temperature, without additives other than the epoxy hardener.

The polymer blend according to the invention is prepared by selecting polymers by recognized techniques. For example, a typical liquid polyester comprises about 40-50% by volume styrene monomer, and preferably about 30% by volume for desired physical properties, and the balance an Ortho or DCPD or an ISO or a blend thereof. The composition does not need to contain a promoter in amounts of about 1-2% by volume of the total composition. This is the standard formulation for making a liquid, general purpose polyester.

In a preferred embodiment of the invention, for most applications contemplated, the epoxy hardener is combined in a volume ratio of from about one part hardener to about two parts of the epoxy and polyester resin volume. The resin combination typically is from about twenty to fifty percent by volume of polyester resin to epoxy resin. Adjustments to the volume ratio can be made but the increase or decrease may change the cure time and change the physical performance of the polymerization.

Extreme changes in volume combinations can cause polymerization not to occur. The epoxy and polyester resins can be blended by hand, but it is recommended that a three part hydro cat pump system with spray head mixer be used. .ine and pot heaters can be added to raise the temperature of the resins; this is not, however, required. This reduces the viscosity of the resins for better movement and mixing as well as speeding cure time. Other exemplary additives include fiberglass mat/cloth, chopper gun, or sand.

The improved composition, in accordance with the invention, can be used alone as a flexible sheet material, can replace many rubber and vinyl applications and demonstrates superior shear strength and improved physical performance under adverse temperature, as well as improved life expectancy. As a lamina, for example, on expanded styrene foam, the material demonstrates superior laminate bonding and delivers structural, impact and wear strength. As an adhesive, the material bonds epoxy products to polyester products and vice versa. It also bonds expanded styrene to itself. As a tile, the polymer can usually take higher than normal volumes (up to about 80-90%) of fillers such as silica sand without losing structural strength, creating a ceramic type material, and is easily handled and installed, with virtually no breakage and the look and wear characteristics of ceramics. The ceramic embodiment usually has color throughout, reducing noticeable scratches. The tile can easily be refinished to restore gloss. The composition can be used alone or with fiberglass reinforcing that will increase strength and reduce the required thickness. Also, the composition will bond to expanded styrene foam insulation and create board stock such as for counters, floors, roofs, walls or fences. As a fire retardant material, the invention with sodium bicarbonate and other known retardant fillers has demonstrated good results, although some wear and structural value may be lost with excessively high volumes of fire retardants. Combinations of known fire retardants without sodium bicarbonate may also be used. Thickening can be accomplished by the addition of sodium

bicarbonate or other powder fillers and silica to create a plaster paste type material. Molding or forming can be accomplished in the polymerized material by the addition of heat. Temperatures over 200° F will noticeably soften the material. As a simulated glass, the polymer resin compositions are usually translucent in color and lend themselves to color agents for a tinted or stained glass type material, although clearer polymer resins are available and useful when clarity is an issue. As a semi-conductor and/or static reducer, the improved composition demonstrates both characteristics when metal flake fillers are used. These are but a few of the many applications of the resin of the invention.

In particular embodiments of the invention, a composition comprising liquid polyester and epoxy is blended for a compatible cure rate, without outside agents other than the hardener in a general ratio by volume of one part hardener to two parts of the combined polyester and epoxy resins; a plural pump spray system is preferred for mixing. The resins can be combined by other methods, including hand batch mixing. Ratios of ingredients can be adjusted to change cure rate and hardness. Additives of silica, fire retardants, U.V. (ultraviolet) stabilizers and absorbers, fiber reinforcing, color agents, and material laminates can also be used.

EXAMPLES:

Example I. An exemplary reaction system for one step application. Two versions are provided; one for a hard material and one for an ultimate flexible material.

Parts by Volume		Component
HARD	FLEXIBLE	
8	4	epoxy resin, such as with bisphenol-A-polyglycidyl ether
2	2	polyester resin, such as with a general purpose resin with less than 50% styrene monomer or gel coat

Parts by Volume		Component
HARD	FLEXIBLE	
5	3	fast epoxy hardener, such as an amino ethyl peperzaine accelerated by nonyl phenol
1-20	1-9	optional components, such as retardants, stabilizers, fillers pigments, and reinforcers
15-25	9-18	Total parts mixed at room temperature (72° F) and one atmosphere pressure.

Example II. To a stirred polymerization container having a capacity of one-half gallon was charged 8 ounces of epoxy resin, Reichhold item 37127, 2 ounces of polyester 31-007-10, and 5 ounces of Epotoph 37610 fast hardener, all from Reichhold. The mixture was stirred and obtained a complete mixture at room temperature (72° F) and at one atmosphere. The mixture was poured onto a flat, mold release waxed mold and allowed to flow to an even thickness of 30 mils. Glass matting was then added to the mixture and styrene foam was laid on top and allowed to cure for 1-4 hours. The item was then released from the mold and allowed the maximum 24 hour cure time. A hardened smooth gloss surface with reinforcement and styrene foam lamination was obtained. Repeating the procedure on the opposite side of the foam provided a structural board stock laminate. Edges would then be added by laminating sheets of the same material, without the foam, using the same resin as adhesive, or the resin was thickened and spread on the edge sides for an encapsulated foam core board stock.

Example III. The above batch mix in Example II using 31-007-10 or general purpose polyester boat resin or gel coat or other esters, were all prepared with an added 80% by weight of silica to the total resin mix and spread to a thickness of 30 mils. Fiberglass mat was added immediately and pressed into the matrix. A ceramic type material was accomplished. Gel coats and/or oxide or other coloring agents are used to produce a colored tile. Higher volumes of silica have also been used but

gloss, smooth finish and structural strength is sometimes lost in higher volume silica fills.

Example IV. To a one gallon batch mixer was added 4 ounces epoxy resin, two ounces polyester resin and 3 ounces Epotoph 37610 fast hardener. A flexible product was produced after cure time. Reinforcement was incorporated in the process for superior strength without loss of flexibility. The product demonstrated superior elasticity even in below freezing temperatures.

Example V. To a triple pump spray system having a ratio of 8:2:5 was charged a mixture of Example I of the above formulations (8 parts epoxy, 2 parts polyester, 5 parts epoxy hardener, by weight). The system employed a spray head mixer. The mixture was combined at the spray head and sprayed onto a flat propylene plastic film to 30 mils.

Again, the was material was released and cured for the maximum 24 hours. In a similar experiment, fiberglass matting was added for a stronger material with comparable results.

Example VI. To the above triple pump spray system in Example V, a fiberglass chopper gun was added to the spray head and like results were accomplished. Also, a silica screw conveyor was added to the spray booth to obtain the ceramic-like material. Additives were included by volume ratio, so that the resin mix would not be changed. Also, sodium bicarbonate flame retardant power and other dry additives were added through the use of the sand blaster without thickening the resins.

Example VII. To a batch mixer, many volume ratios were tried. In principle, the following general guidelines have evolved when the use of outside curing agents are not employed:

1. From a volume ratio of polyester and epoxy, half as much polyester as epoxy may be used with good polymerization results. Amounts over a one-half to one volume ratio of polyester to epoxy can result in long polymerization times or failed polymerization.

The preferred hardeners are known epoxy resin hardeners. These are generally recommended by their

manufacturers to be for epoxy resins only, and in a ratio of two parts resin to one part hardener. However, it has been determined that up to one part extra hardener per two parts polyester will cure and cross-link the epoxy/polyester precursors. The following examples have volume numbers, demonstrating this. Each digit equals the part ratios in the order () epoxy () polyester () hardener:

Formula 423 produces a flexible material.

Formula 312 produces a semi-hard material.

Formula 825 produces a rigid material.

The present invention has been disclosed as an improved composition that results in a plastic material that has multiple uses. Primarily, an improved composition consists of predetermined ratios by volume of liquid epoxy resin and polyester resin with a suitable hardener to produce a superior plastic material whose flexibility or hardness can be varied by the ratios used between the epoxy and the polyester and the hardener.

Another very important use for the improved composition in accordance with the present invention, consisting of epoxy resin and polyester resin and a suitable hardener, is the use with block or sheets of expanded styrene foam with the improved composition in accordance with the invention for a protective surface that readily bonds to the expanded styrene surface without destroying the foam, allowing sheets of styrene foam to be coated with a rigid protective epoxy/polyester material for increasing the overall strength of the styrene foam and encasing it in a protected environment. One of the most important characteristics of the present invention is its ability to bond to expanded styrene. Another very important use is an adhesive either with elastomeric or rigid properties, particularly applicable to styrene bonding and epoxy to polyester bonding.

Finally, an important use of the present invention is as a material comprising cross-linked and cured epoxy resin and polyester resin for simulating suitable, known thermoset plastics, by, for example, incorporating high filler such as

silica sand to provide a ceramic stucco or brick simulation, or a filler such as fiberglass fibers to provide enhanced strength, or alone as a translucent product to simulate the look of glass.

In summary, the composition of the invention is truly a unique composition of epoxy resin and polyester resin which forms a material having a large number of multiple uses and which reduces construction cost in the use of comparable materials.

The instant invention has been shown and described herein in what is considered to be the most practical and preferred embodiment. It is recognized, however, that departures may be made therefrom within the scope of the invention and that obvious modifications will occur to a person skilled in the art.

CLAIMS

What Is Claimed Is:

1. A sheet of a cured epoxy resin cross-linked with a polyester.

2. The sheet of claim 1, having a thickness of at least about 1/32 inch.

3. The sheet of claim 2, laminated to expanded styrene foam.

4. The sheet of claim 1 which is flexible.

5. The sheet of claim 1 which is rigid.

6. The sheet of claim 1 which is molded.

7. The sheet of claim 1, produced from a composition consisting essentially of liquid epoxy resin, liquid polyester, and a hardener for the epoxy resin, cross-linked and cured at about room temperature.

8. The sheet of claim 7, wherein the hardener is an amino ethyl peperzaine accelerated by nonyl phenol.

9. The sheet of claim 7, wherein the polyester resin includes styrene moieties.

10. The sheet of claim 9, bonded to styrene foam.

11. The sheet of claim 1, further including a filler, a colorant, a reinforcing agent, or a fire retardant.

12. The sheet of claim 1, further including sand.

13. The sheet of claim 1, further including fiberglass.

14. A laminate comprising expanded styrene foam bonded to the sheet of claim 1.

15. The laminate of claim 14, produced by applying a composition consisting essentially of liquid epoxy resin, liquid polyester resin and epoxy hardener to a expanded styrene foam lamina, and curing and cross-linking the composition at room temperature.

16. The laminate of claim 15, wherein a reinforcing agent is introduced into the composition prior to curing.

17. The laminate of claim 16, wherein the reinforcing agent is fiberglass.

18. The laminate of claim 15, which is a structural element.

19. A bonding agent comprising a composition consisting essentially of liquid epoxy resin, liquid polyester, and a hardener for the epoxy resin, curable at room temperature.

20. The bonding agent of claim 19, wherein the polyester resin contains styrene moieties.

21. The laminate of claim 15, wherein the cross-linked epoxy/polyester lamina is at least about 1/32" thicker.

22. The sheet of claim 1, further including sodium bicarbonate.

23. A simulated tile comprising a cured epoxy resin cross-linked with a polyester resin.

24. The simulated tile of claim 23, further including a filler.

25. The simulated tile of claim 24, wherein the filler is sand.

26. The simulated tile of claim 24 wherein the filler is present in an amount of at least 60% by volume of the total resin content.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/11254

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C08F 20/00, 283/00
US CL :525/438, 530, 533
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 525/438, 530, 533

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS SEARCH: EPOXY, POLYEPOXY, POLYESTER, CROSSLINK CHEMICAL ABSTRACTS AND JAPANESE ABSTRACTS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 5,177,159 (STEINMANN ET AL.) 05 January 1993, see entire document.	1, 4-7, 9, 11, 13,19,20, 23-26 ---------- 2,3,8,10,12 14-18,21, 22
X ---- Y	US, A, 4,076,767 (SAMEJIMA) 28 February 1978, see entire document.	1,4-7,9,11, 13,,19,20, 23-26 ---------- 2,3,8,10, 12,14-18, 21,22

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
16 NOVEMBER 1994

Date of mailing of the international search report
21 FEB 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
JOHN C. BLEUTGE

Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/11254

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	(LEE, ET AL.) "HANDBOOK OF EPOXY RESINS", 1982 REISSUE, BY McGRAW-HILL BOOK CO. (US), see pages 7-20 and 14-2.	8,11,12,25